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(1)

SOLID PROPELLANT RESEARCH OPERATIONS
OF THE SOLID ROCKET PLANT AT AZUSA

(6) INVESTIGATION OF THE MECHANISMS
OF DECOMPOSITION, COMBUSTION, AND DETONATION
OF SOLIDS

A Report To

DIRECTOR OF AERONAUTICAL SCIENCES
AIR FORCE OFFICE OF AEROSPACE RESEARCH

(15) Contract AF 49(638)-851

OSR Project No. 9750, Task 37501

(16) ARPA Order No. 24-60, Proj. 4759

(14) Report No. 0372-01-14 / June 1963 / Copy No. 3

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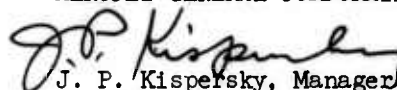
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This is the fourteenth Technical Operating Report submitted in partial fulfillment of the contract. It covers the period 1 April through 30 June, 1963.

AEROJET-GENERAL CORPORATION



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(Azusa)

ABSTRACT

\downarrow
~~Apparent flame strengths~~ ^{$NH_3 - O$} for the ~~ammonia-oxygen~~ ^{$NH_3 - O - Cl$} and ~~ammonia-oxygen-chlorine~~
 reactions have been determined as a function of reactor pressure, using the opposed-jet technique and 0.77-cm-ID nozzles. It has been shown that the ~~ammonia-oxygen~~ ^{$NH_3 - O$} flame strength is dependent on the square of the reactor pressure when both 0.46- and 0.77-cm jets are used. The proportionality of the flame strength with the diameter of the jet, which is required by theory, has also been demonstrated.

^{NH_3} Apparent flame strength ^{$O - Cl$} measurements for ~~ammonia~~ as fuel, with ~~oxygen-chlorine~~ mixture as oxidizer, have been made at 300, 450, 600 and 745 torr. The flame strength was inversely proportional to the mass fraction of Cl_2 ^{Cl} in the mixture. Extrapolations to zero flame strength indicated that no flame is possible at mass fractions of ~~chlorine~~ ^{Cl} of approximately 0.5.

^{Cl} Analyses of the data for ~~ammonia-oxygen-chlorine~~ ^{$NH_3 - O - Cl$} systems indicate that ~~chlorine~~ does not act as a diluent but competes with ~~oxygen~~ ^{O} in reaction with NH_3 . The three-component system also shows flame strength dependence on the square of the reactor pressure.

\nwarrow

I. INTRODUCTION

The objective of the research being conducted under this contract, funded by the Advanced Research Projects Agency, is to obtain a better understanding of the mechanisms of combustion, decomposition, and detonation of solids. Current investigations are concerned with the gas-phase reactions associated with the combustion of composite solid propellants and their relationship to the energy transport processes near propellant surfaces.

II. TECHNICAL STATUS

A. SUMMARY OF PREVIOUS WORK

A series of gas-phase reactions believed to occur above the surface of decomposing or burning ammonium perchlorate-oxidized composite propellants are being examined. The reactions of ammonia with perchloric acid were carried out, using both flow and batch techniques. The reaction between propane and air was also studied, using the opposed-jet technique. The combustion of the ammonia-oxygen and the ethylene-oxygen systems have also been examined by the same technique.

1. Opposed-Jet Flame Studies of the Ammonia-Oxygen Reactions

On the basis of the mechanism of ammonium perchlorate combustion which was reviewed in the previous report (Report No. 0372-01-13, on Contract AF 49(638)-851, dated 31 March 1963) studies of the reactions of oxygen and chlorine with ammonia are being carried out at flame temperatures. The apparent flame strength which is a measure of the limiting chemical reaction rate has been determined for the opposed-jet reaction of oxygen with ammonia between 250 and 760 torr. A jet diameter of 0.46 cm was used in these

determinations. A plot of the apparent flame strength of this reaction against the square of the reactor pressure was linear which indicated that the reaction is approximately a second order function of pressure overall.

On the basis of a theoretical study by Spalding (Ref. 1) the volumetric consumption rate of ammonia in the reaction was computed.



An approximate value of $4.5 \text{ g/cm}^3\text{-sec}$ was obtained. This corresponds to a volumetric heat release rate of approximately $2.4 \times 10^4 \text{ cal/cm}^3\text{-sec}$. More exact calculations will require the computer solutions to Spalding's equations.

The value of the apparent flame strength at one atmosphere was used to estimate the mass burning rate for a stoichiometric mixture of oxygen and ammonia, utilizing the approximate theory of laminar flame propagation derived by Zeldovich and Frank-Kamenetsky. The value derived from the apparent flame strength was within 15% of a value derived from a measurement of flame speed by Ausloos and Van Tiggelen (Ref. 2). In view of the approximations employed in these computations, the comparison is deemed more than satisfactory.

2. Combustion of Ethylene with Air

The ethylene-air combustion was studied as a prototype reaction for testing the opposed-jet reactor and also as an example of the reaction of a typical binder gas with air. A plot of the apparent flame strength of this system as a function of reactor pressure indicated a total reaction order of two. A volumetric rate of ethylene consumption at one atmosphere was calculated to be $1.8 \times 10^{-1} \text{ g/cm}^3\text{-sec}$ from the apparent flame strength value of $0.19 \text{ g/cm}^2\text{-sec}$. The corresponding heat-release rate was $2.2 \times 10^3 \text{ cal/cm}^3\text{-sec}$.

3. Combustion of Ammonia with Oxygen-Chlorine Mixtures

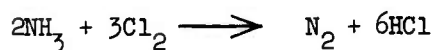
Initial experiments had been carried out with the system: ammonia vs oxygen-chlorine. The opposed-jet technique was employed in this work. Quantitative measurements were considerably more difficult to obtain than in

the absence of chlorine. New mixing and flow control equipment was installed to improve the reproducibility of these measurements.

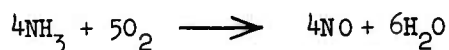
B. CURRENT AND PLANNED WORK

1. Combustion of Ammonia with Oxygen-Chlorine Mixtures

The proposed mechanism for the gas-phase combustion reactions above decomposing ammonium perchlorate surfaces has been indicated to be dependent kinetically on a competition between the two reactions:



and



This proposed mechanism has been covered in detail previously (Refs. 3 and 4).

In order to test this tentative mechanism, an investigation of the flame reaction between ammonia and a mixture of oxygen and chlorine is being carried out by the opposed-jet technique. This technique has been described previously (Refs. 3, 5, 6, 7).

Table 1 is a tabulation of the apparent flame strengths for the ammonia-oxygen systems as a function of reactor pressure. These data were obtained using 0.77-cm-ID nozzles. The data which were obtained at pressures from 100 to 600 torr have been plotted in Figure 1 against the square of the reactor pressure in atmospheres. The previously reported data obtained with a nozzle diameter of 0.46 cm are included for comparison. The oxygen-ammonia flame data have been used as a base line reference for the chlorine-oxygen-ammonia studies which are reported below. As is indicated by the linear nature of the two sets of data when plotted against the square of the reactor pressure, the overall second order nature of the pressure dependence holds for both nozzle diameters.

The data recorded in Table 1 and Figure 1 (and all data in this report) have been calculated using the assumption of laminar flow.

However, the Reynolds Numbers of the fuel flow with the 0.77-cm-ID nozzles are generally in excess of 2000. If these data are recalculated assuming turbulent flow conditions, the proportionality of the apparent flame strength with the diameter of the jet may be shown as indicated by Spalding (Ref. 1).

Apparent flame strength measurements for ammonia-oxygen-chlorine systems are collected in Tables 2 through 5 at pressures of 300, 450, 600, and 745 torr. These data exhibit considerably more scatter than those for systems without chlorine.

Figures 2 through 5 are plots of the apparent flame strength data against the mass fraction of chlorine in the initial reaction mixture. These figures indicate that the apparent flame strength of ammonia-oxygen-chlorine systems decreases linearly as the mass fraction of chlorine increases. Extrapolation of these data at all pressures to zero flame strength indicates that, at mass fractions of chlorine of approximately 0.45 to 0.50, no flame is possible. The meaning of this value requires further investigation.

Spalding (Ref. 1) has pointed out that the apparent flame strength ($\rho_{\infty} U_{\text{ext}}$) is a direct linear function of f , the mass fraction of material derived from the fuel-bearing stream which is present in the local mixture. The linear dependence of the apparent flame strength on the mass fraction of chlorine may be explained if the function of the chlorine in the reaction is to remove, in effect, a portion of the ammonia from the ammonia-oxygen reaction, thus decreasing the value of f . A development of the flame strength concept in terms of reacting proportions (molar units) is planned in order to clarify the meaning of the decrease of flame strength as a function of chlorine content. This development should result in an explanation of the effect of inhibiting components on flame strength.

Figure 6 is a plot of the mass ratio of oxygen-to-ammonia against the mass fraction of chlorine, in the reaction mixture for data obtained at 745 torr. It demonstrates that the oxygen to ammonia ratio required for axial extinguishment decreases linearly as the mass fraction of chlorine is increased. An examination of oxygen-ammonia flame strength data at all pressures has indicated

as expected, that the mass ratio of oxygen to ammonia is constant within the experimental limits. From Figure 6 it may be concluded that chlorine is not acting as a diluent but is engaged in a competition with oxygen for the fuel, ammonia. In addition, it is implied that the mechanism of chlorine reaction in the flame is consistent under all conditions.

Figure 7 is a plot of the mass ratio of the total oxidizer stream to the fuel stream against the mass fraction of chlorine for the data obtained at 745 torr. Despite the scatter of the data, the positive slope of the linear dependence shows that the ratio increases with chlorine content. In addition to confirming the conclusions of the preceding paragraph, this plot suggests that the order of the reaction between chlorine and ammonia is greater than that between oxygen and ammonia. Confirmation of this latter point will require further data analyses at all pressures. Verwimp and Van Tiggelen (Ref. 8) have indicated that although the overall reaction order is about 1.7 in the temperature range between 490 and 540°C that the reaction is 0.3 order in oxygen.

Figure 8 shows the apparent flame strength of ammonia-oxygen and ammonia-oxygen-chlorine flames at four chlorine mass fractions: 0, 0.1, 0.2, and 0.3, all plotted against the square of the reactor pressure. The apparent flame strength appears to depend on the second order of the pressure at all levels. However, the inhibiting effect of chlorine on the flame strength is clearly demonstrated.

Figure 9 is a plot of the slopes obtained from Figures 2 through 5 against the square of reactor pressure. The ordinate indicates how much the apparent flame strength is modified by increasing the chlorine mass fraction. The linearity of the plot demonstrates a second order dependence of pressure on the chlorine effect.

2. Future Work

In the immediate future, further examination of the ammonia-oxygen-chlorine reaction is planned in order to establish a probable mechanism which will account for the observed effects of chlorine.

A theoretical analysis of the theory of flame strength in terms of chemical kinetic units will be initiated.

An examination of the reaction between ammonia and nitric oxide will be initiated in order to compare known kinetic data with flame study data obtained by the opposed-jet technique.

III. PROJECT PERSONNEL

During the period covered by the report, the following personnel contributed the indicated approximate portions of their time to the program.

	<u>Time, %</u>
D. J. Sibbett, principal investigator	90
R. F. Chaiken, consultant	30
F. J. Cheselske, research chemist	30
R. S. Dodds, senior laboratory technician	100

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1. D. B. Spalding, "Theory of Mixing and Chemical Reaction in the Opposed-Jet Diffusion Flame," ARS Jour. 31, 763-771 (1961).
2. P. Ausloos and A. Van Tiggelen, Bull. Soc. Chim. Belges 60, 433 (1951).
3. Proposal to the Air Force Office of Aerospace Research for a Continued Investigation of the Mechanisms of Decomposition, Combustion and Detonation of Solids, Aerojet-General Corporation, Proposal SR-62859, December 1962.
4. Twelfth and Thirteenth Quarterly Reports on Contract AF 49(638)-851, dated 31 December 1962 and 31 March 1963; program entitled, Investigation of the Mechanisms of Decomposition, Combustion and Detonation of Solids.
5. A. E. Potter, J. Heimerl, and J. N. Butler, "Apparent Flame Strength," Eighth Symposium (International) on Combustion, Williams and Wilkins Co., Baltimore 1962, p. 1027-34.
6. E. Anagnostou and A. E. Potter, "Flame Strength of Propane-Oxygen Flames at Low Pressures in Turbulent Flow," Ninth Symposium (International) on Combustion, Academic Press, New York, 1963, p. 1-6.
A. E. Potter and J. N. Butler, ARS Jour. 29, 54-60 (1959).
8. J. Verwimp and A. Van Tiggelen, Bull. Soc. Chim. Belges 62, 205 (1953).

TABLE 1

AMMONIA-OXYGEN FLAMES

[Apparent Flame Strength (AFS)
Nozzle: 0.77-cm-ID]

<u>AFS Laminar Flow g/cm²-sec</u>	<u>AFS Turbulent Flow g/cm²-sec</u>	<u>Reactor Pressure torr</u>
1.36	0.829	600
1.30	0.793	
0.798	0.487	400
0.787	0.480	
0.794	0.484	
0.320	0.195	300
0.343	0.209	
0.336	0.205	
0.403	0.246	
0.289	0.176	250
0.284	0.173	
0.265	0.162	
0.169	0.103	200
0.172	0.105	
0.126	0.077	150
0.126	0.077	
0.078	0.048	100
0.080	0.049	

TABLE 2

$\text{NH}_3\text{-O}_2\text{-Cl}_2$ SYSTEM
AT 745 TORR
(Nozzle: 0.768 Cm ID)

<u>AFS</u> <u>g/cm²-sec</u>	<u>Mass Fraction</u> <u>of Cl₂ in</u> <u>Mixture</u>	<u>Mass Fraction</u> <u>of O₂ in</u> <u>Oxidizer</u>
2.01	0.0683	0.872
1.83	0.101	0.812
1.80	0.109	0.802
1.72	0.147	0.723
1.62	0.138	0.747
1.47	0.179	0.668
1.42	0.186	0.668
1.21	0.225	0.600
1.19	0.225	0.600
0.989	0.284	0.503
0.968	0.287	0.500
0.866	0.313	0.450
0.852	0.314	0.453
0.844	0.300	0.460
0.844	0.300	0.460
0.838	0.302	0.466
0.722	0.337	0.390
0.717	0.353	0.394

TABLE 3 $\text{NH}_3\text{-O}_2\text{-Cl}_2$ SYSTEM

AT 600 TORR

(Nozzle: 0.768 Cm ID)

<u>AFS</u> <u>g/cm²-sec</u>	<u>Mass Fraction</u> <u>of Cl₂ in</u> <u>Mixture</u>	<u>Mass Fraction</u> <u>of O₂ in</u> <u>Oxidizer</u>
1.28	0.0734	0.861
1.21	0.0663	0.878
1.20	0.0708	0.872
1.15	0.132	0.751
1.06	0.118	0.786
0.922	0.207	0.647
0.894	0.156	0.560
0.744	0.222	0.592
0.740	0.274	0.543
0.732	0.210	0.610
0.716	0.252	0.507
0.656	0.226	0.557
0.532	0.300	0.464
0.528	0.337	0.436
0.516	0.297	0.473

TABLE 4 $\text{NH}_3\text{-O}_2\text{-Cl}_2$ FLAMES

AT 450 TORR

(Nozzle: 0.768 Cm ID)

<u>AFS</u> <u>g/cm²-sec</u>	<u>Mass Fraction</u> <u>of Cl₂ in</u> <u>Mixture</u>	<u>Mass Fraction</u> <u>of O₂ in</u> <u>Oxidizer Stream</u>
0.732	0.0490	0.903
0.730	0.0551	0.894
0.716	0.0283	0.931
0.708	0.0771	0.865
0.668	0.0710	0.863
0.658	0.0524	0.897
0.614	0.0733	0.855
0.578	0.106	0.802
0.546	0.8022	0.838
0.545	0.121	0.792
0.520	0.124	0.779
0.497	0.152	0.728
0.468	0.152	0.701
0.446	0.210	0.629
0.445	0.209	0.630
0.442	0.204	0.637
0.424	0.182	0.637
0.402	0.209	0.654
0.386	0.233	0.604
0.380	0.221	0.619
0.371	0.223	0.645
0.347	0.261	0.560
0.326	0.262	0.576

Table 4

TABLE 5

$\text{NH}_3\text{-O}_2\text{-Cl}_2$ FLAMES

AT 300 TORR

(Nozzle: 0.768 Cm ID)

<u>AFS</u> <u>g/cm²-sec</u>	<u>Mass Fraction</u> <u>of Cl₂ in</u> <u>Mixture</u>	<u>Mass Fraction</u> <u>of O₂ in</u> <u>Oxidizer² Stream</u>
0.326	0.0488	0.910
0.304	0.0511	0.907
0.290	0.0942	0.827
0.254	0.100	0.822
0.251	0.105	0.780
0.220	0.189	0.664
0.209	0.190	0.681
0.169	0.257	0.550

AMMONIA-OXYGEN FLAMES

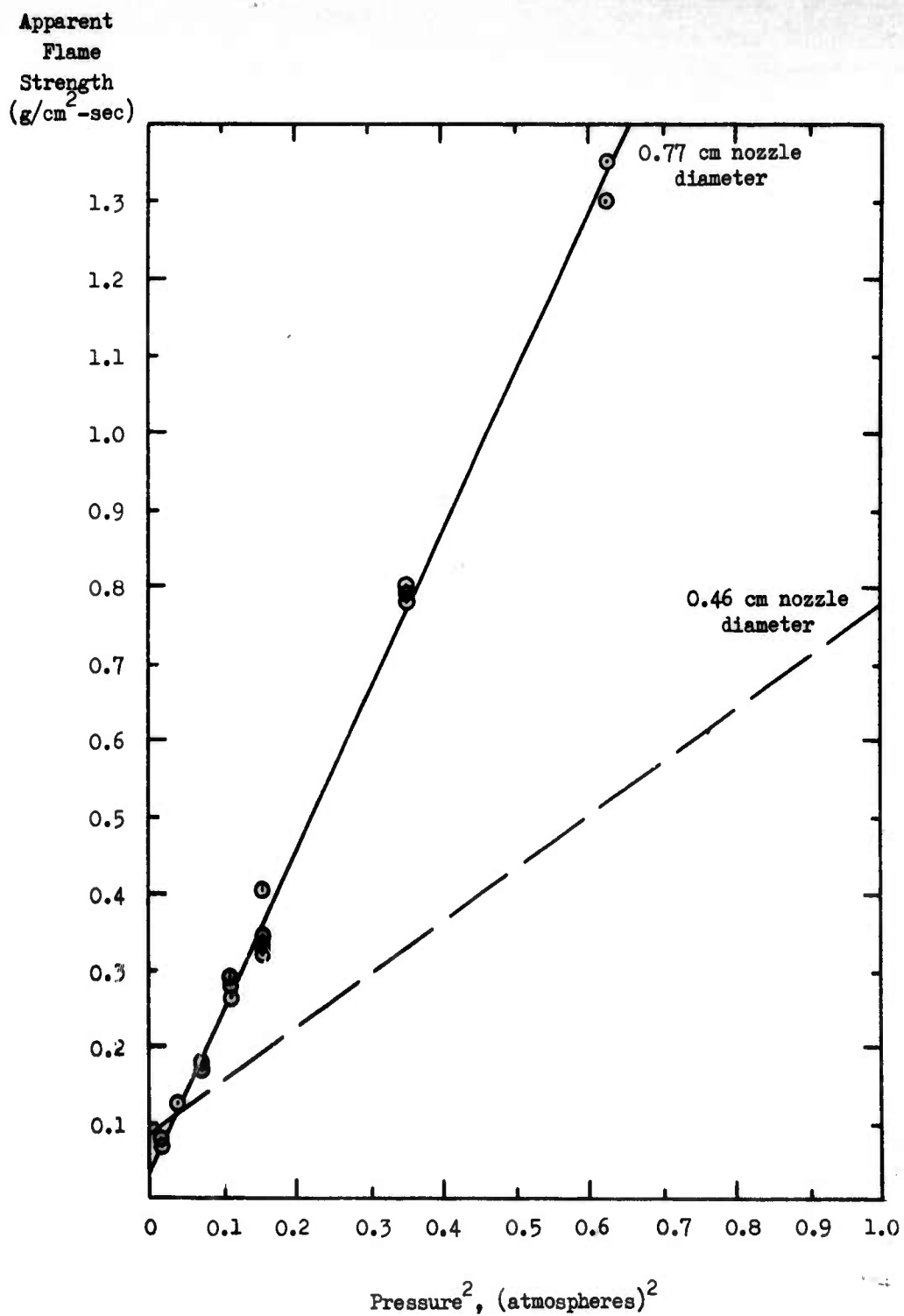


Figure 1

AMMONIA-OXYGEN-CHLORINE FLAMES

Apparent
Flame
Strength
($\text{g}/\text{cm}^2\text{-sec}$)

Pressure: 745 torr.
Nozzle: 0.77 cm

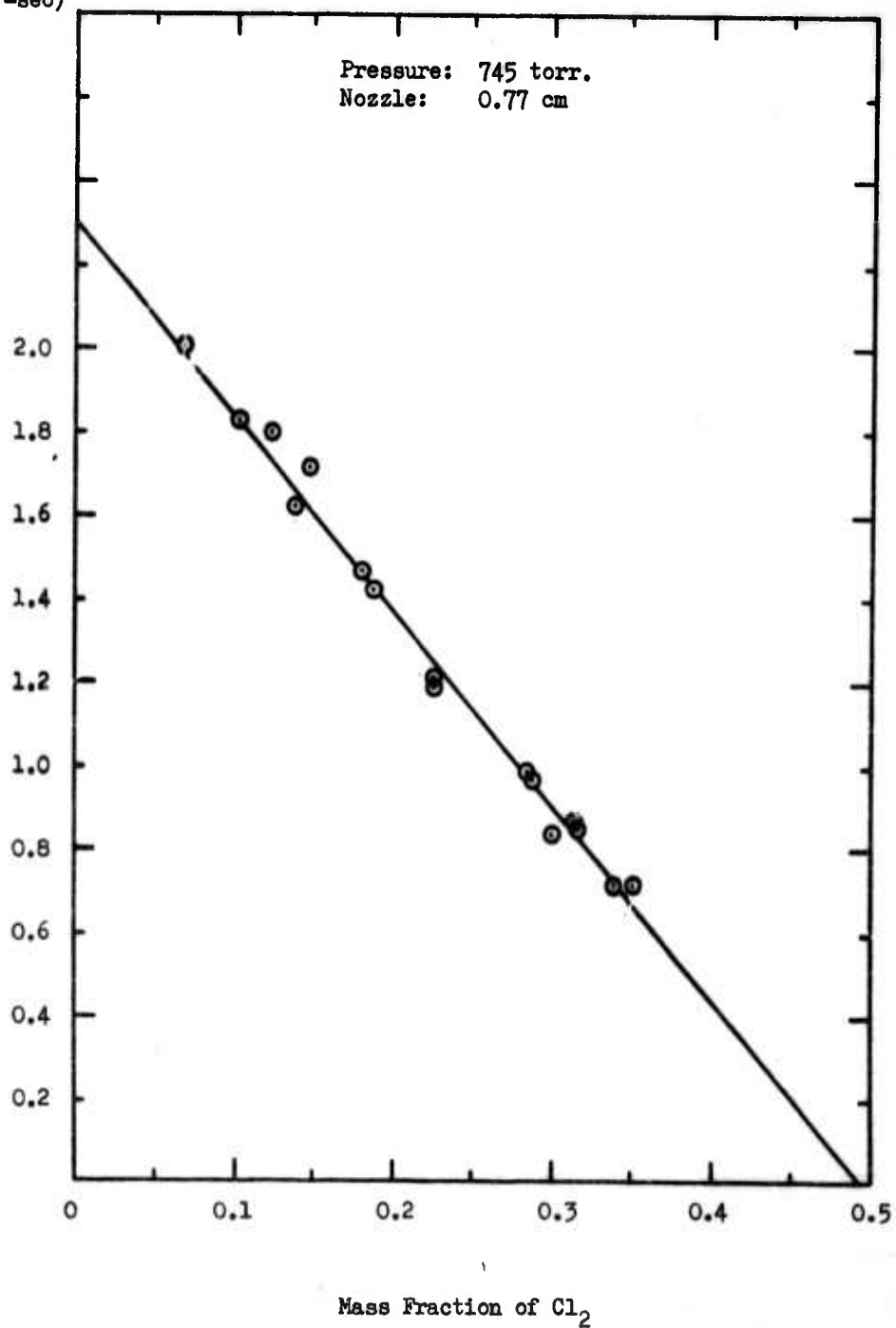


Figure 2

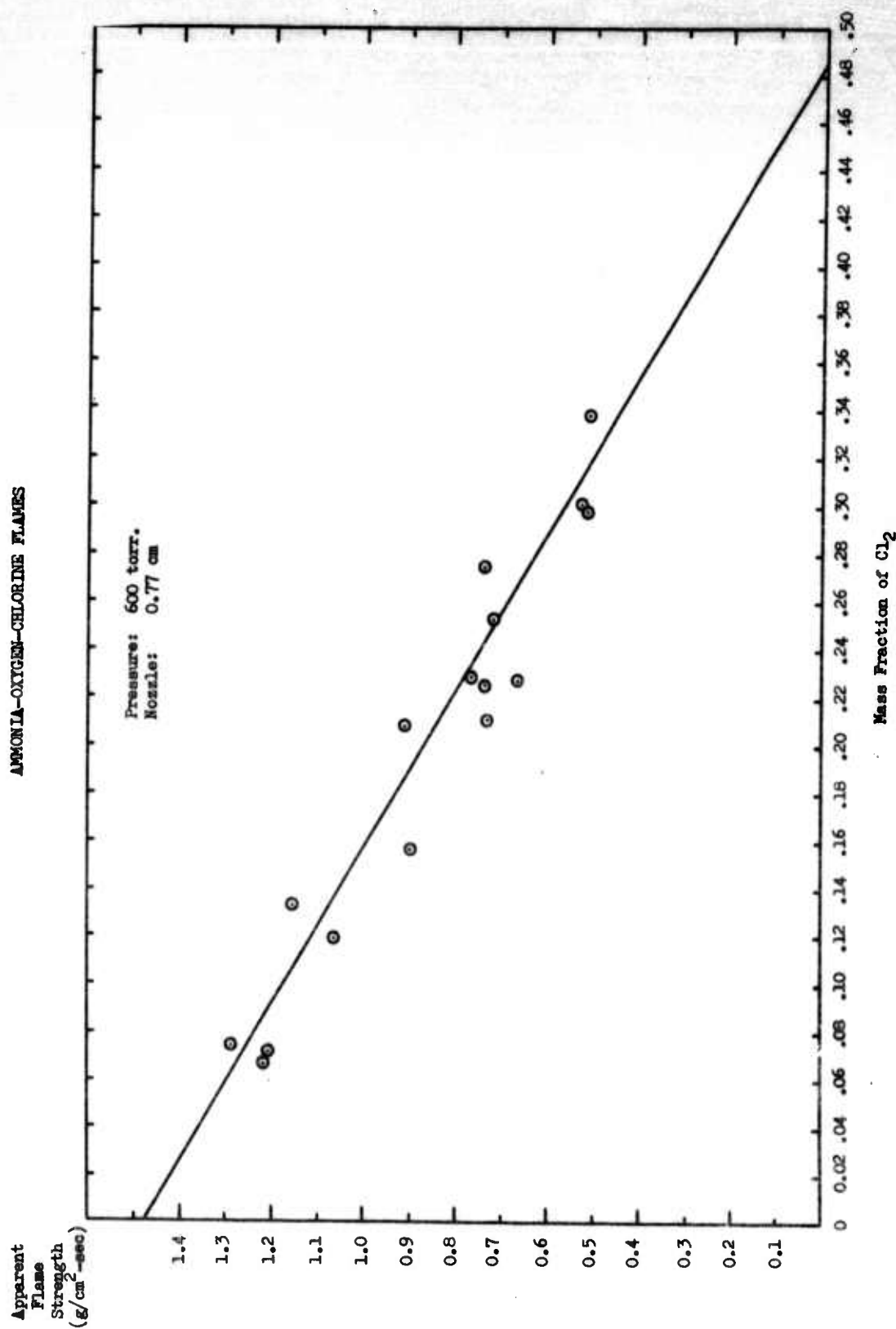


Figure 3

AMMONIA-OXYGEN-CHLORINE FLAMES

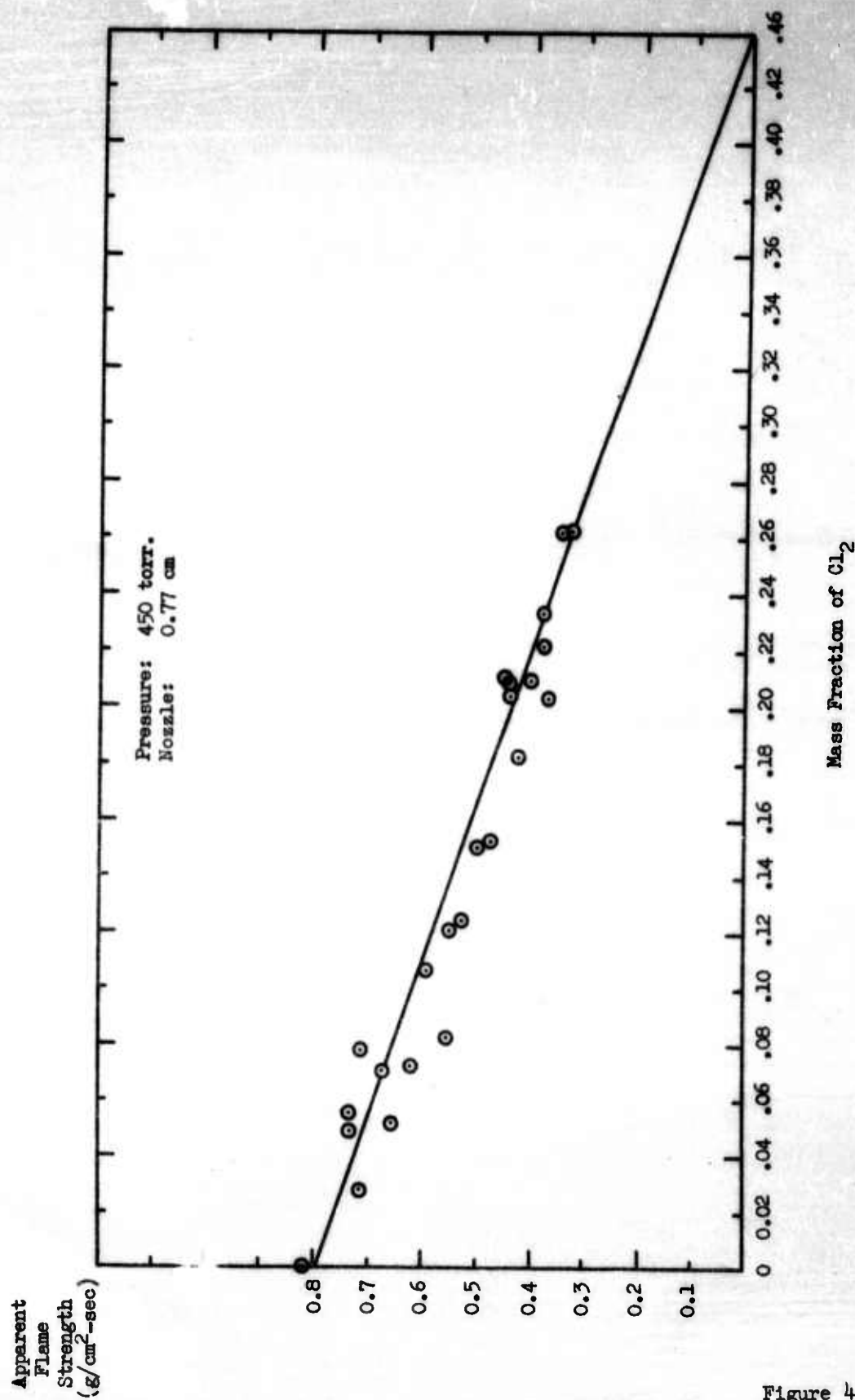


Figure 4

AMMONIA-OXYGEN-CHLORINE FLAMES

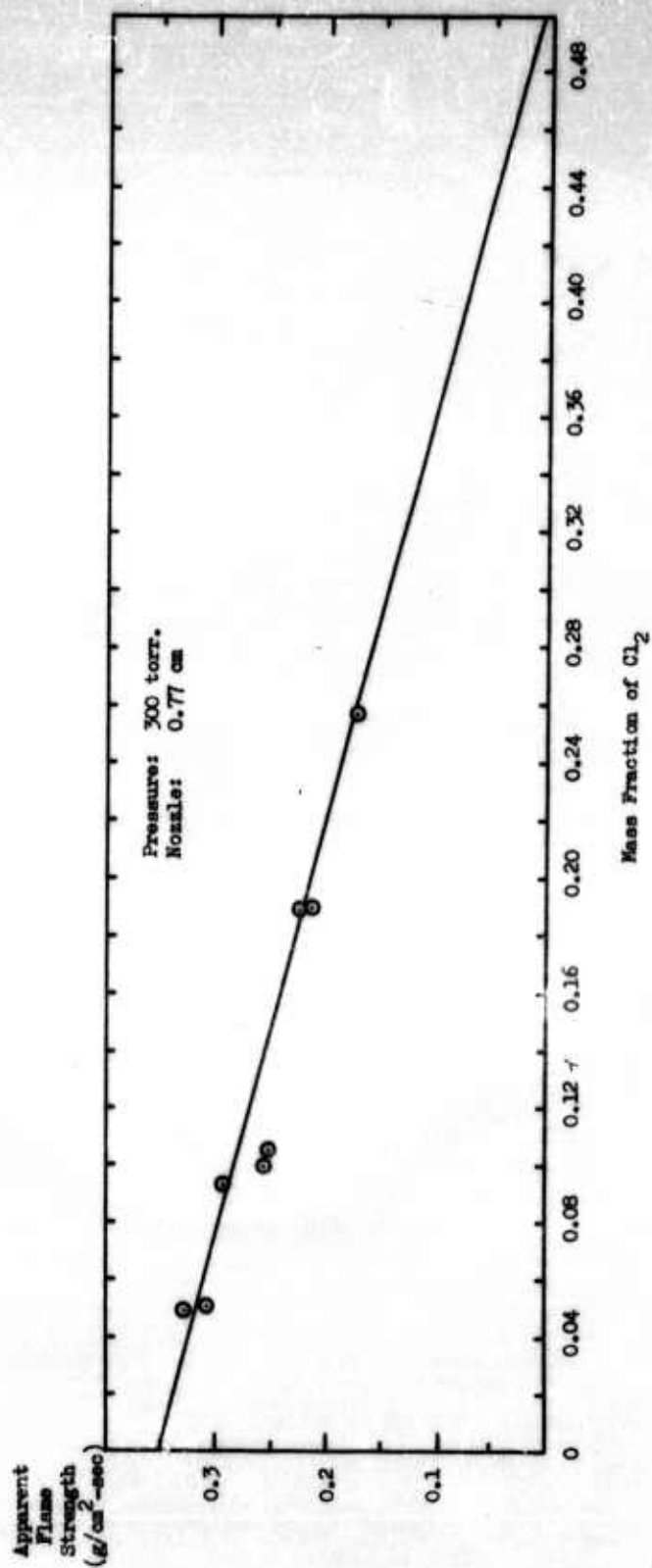


Figure 5

AMMONIA-OXYGEN-CHLORINE FLAMES

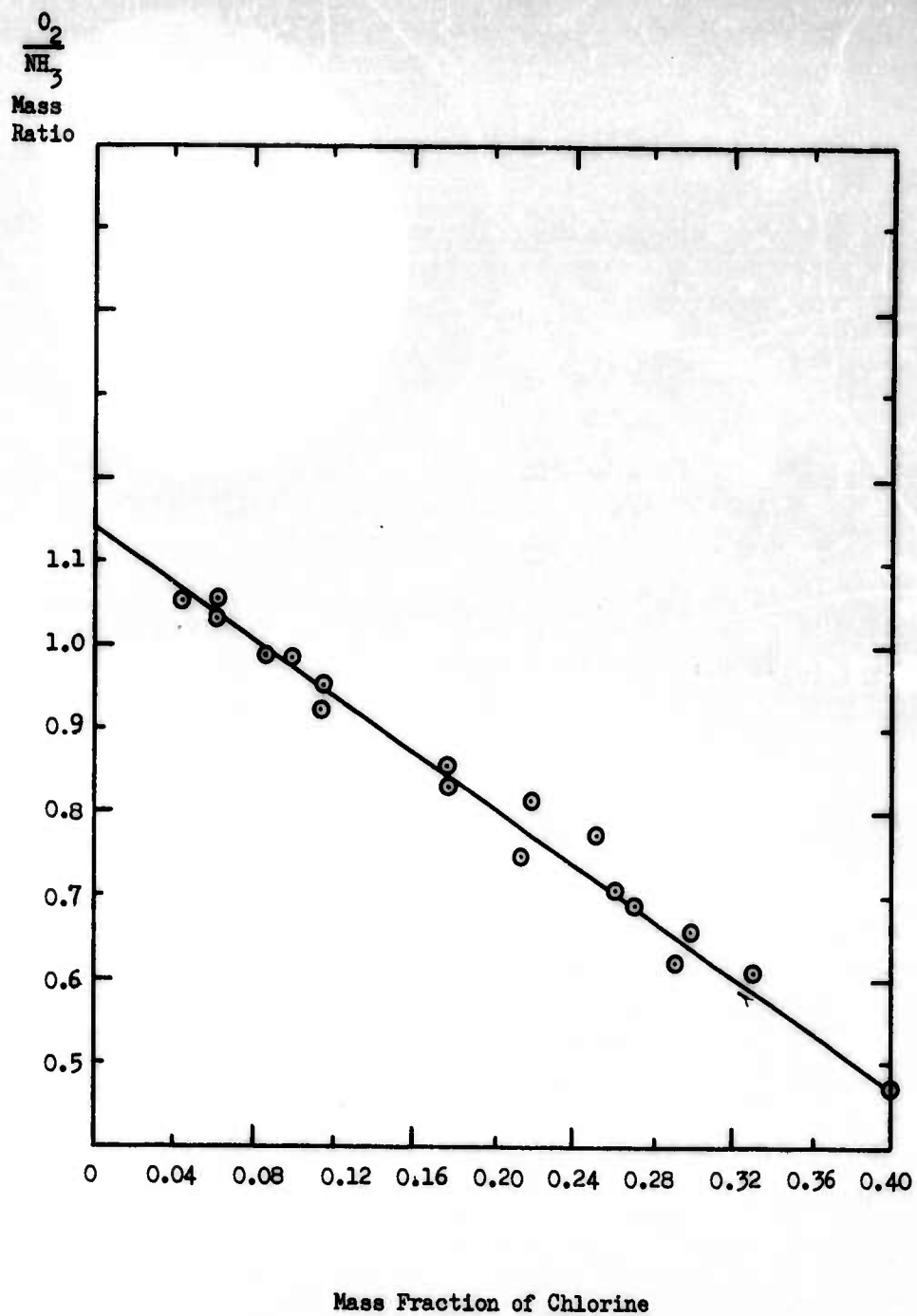
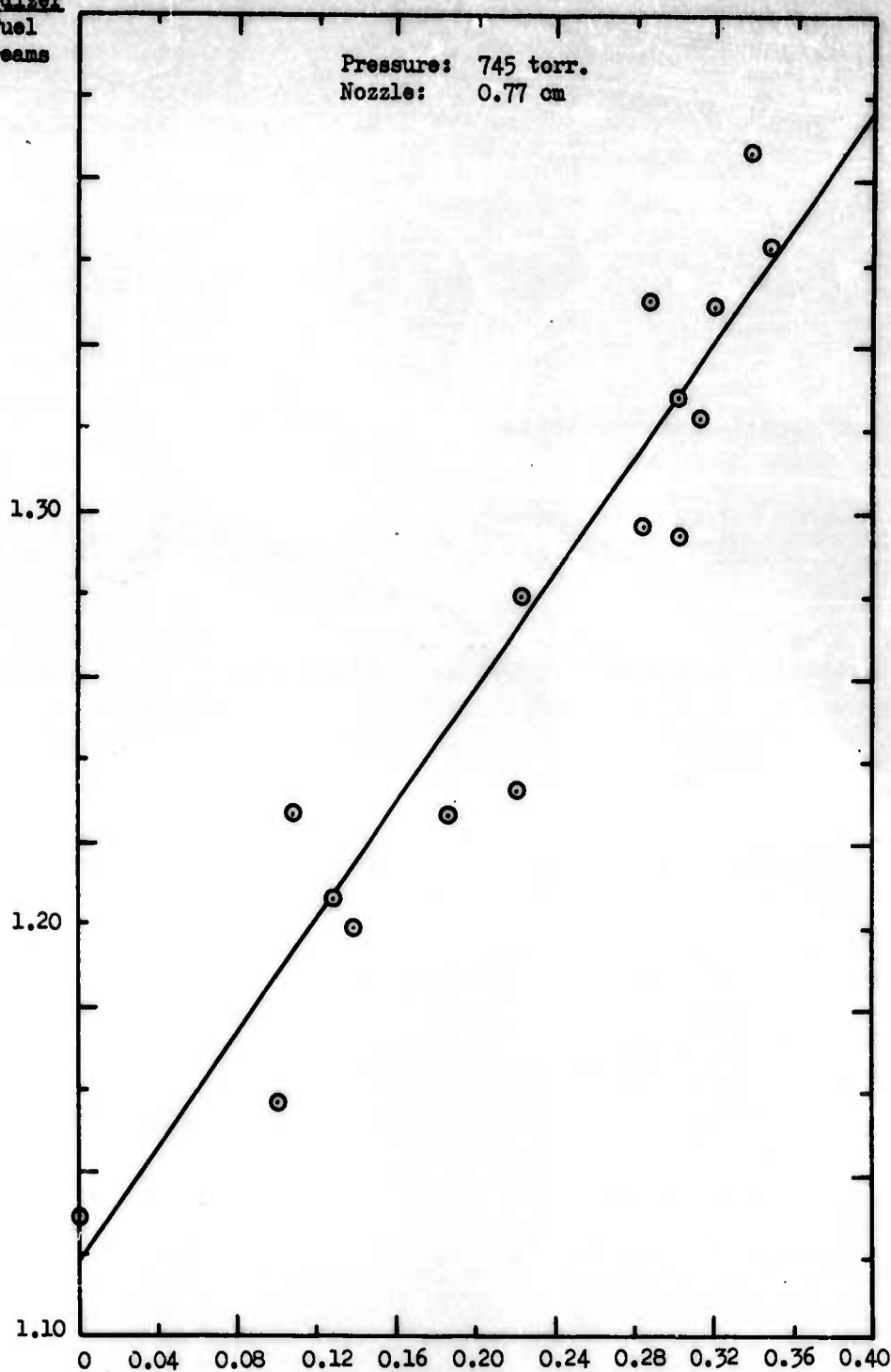


Figure 6

AMMONIA-OXYGEN-CHLORINE FLAMES

Mass
Ratio
Oxidizer
Fuel
Streams



Mass Fraction of Chlorine

Figure 7

AMMONIA-OXYGEN-CHLORINE FLAMES

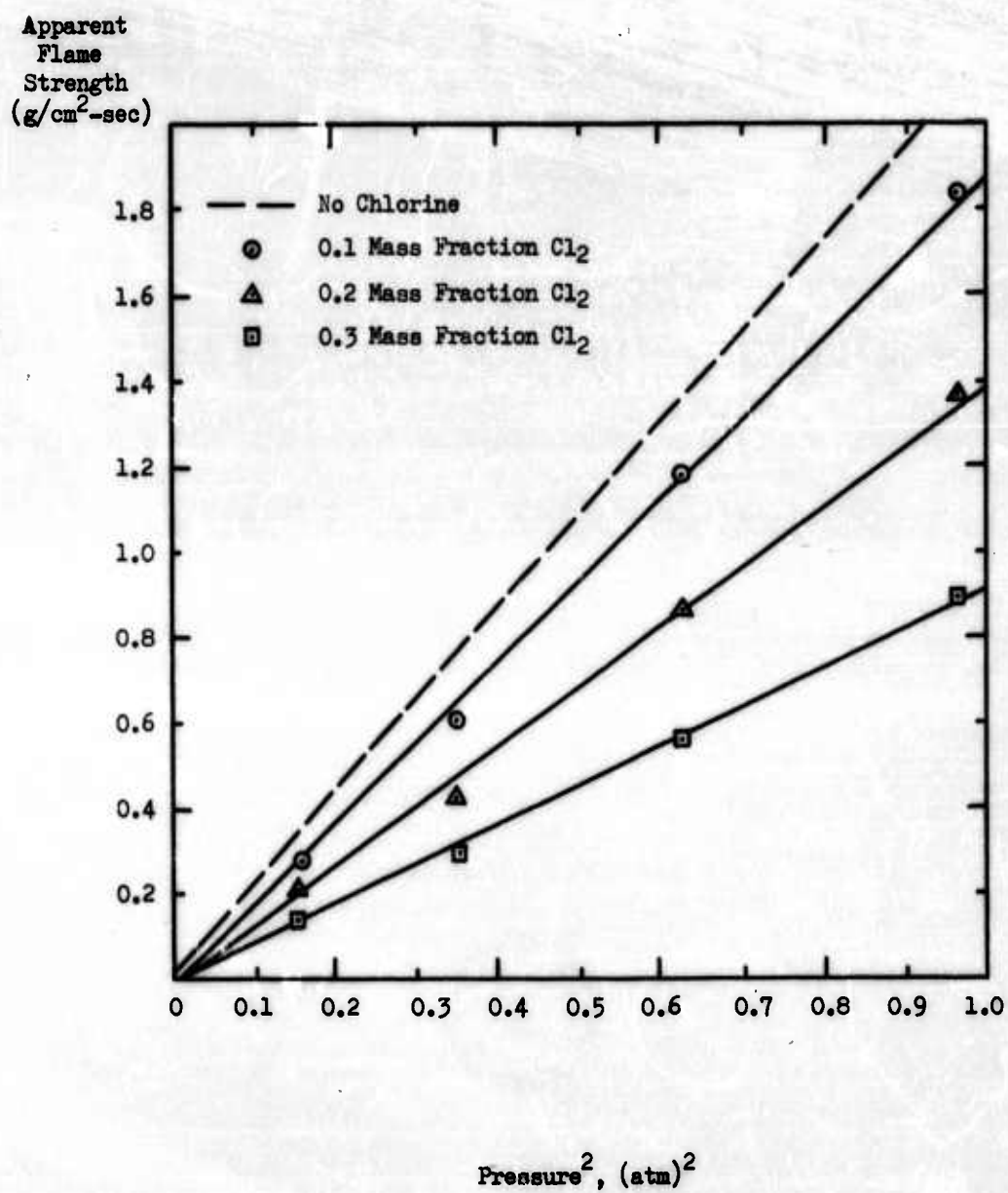


Figure 8

AMMONIA-OXYGEN-CHLORINE FLAMES

Slope AFS vs
Mass Fraction
of Cl_2

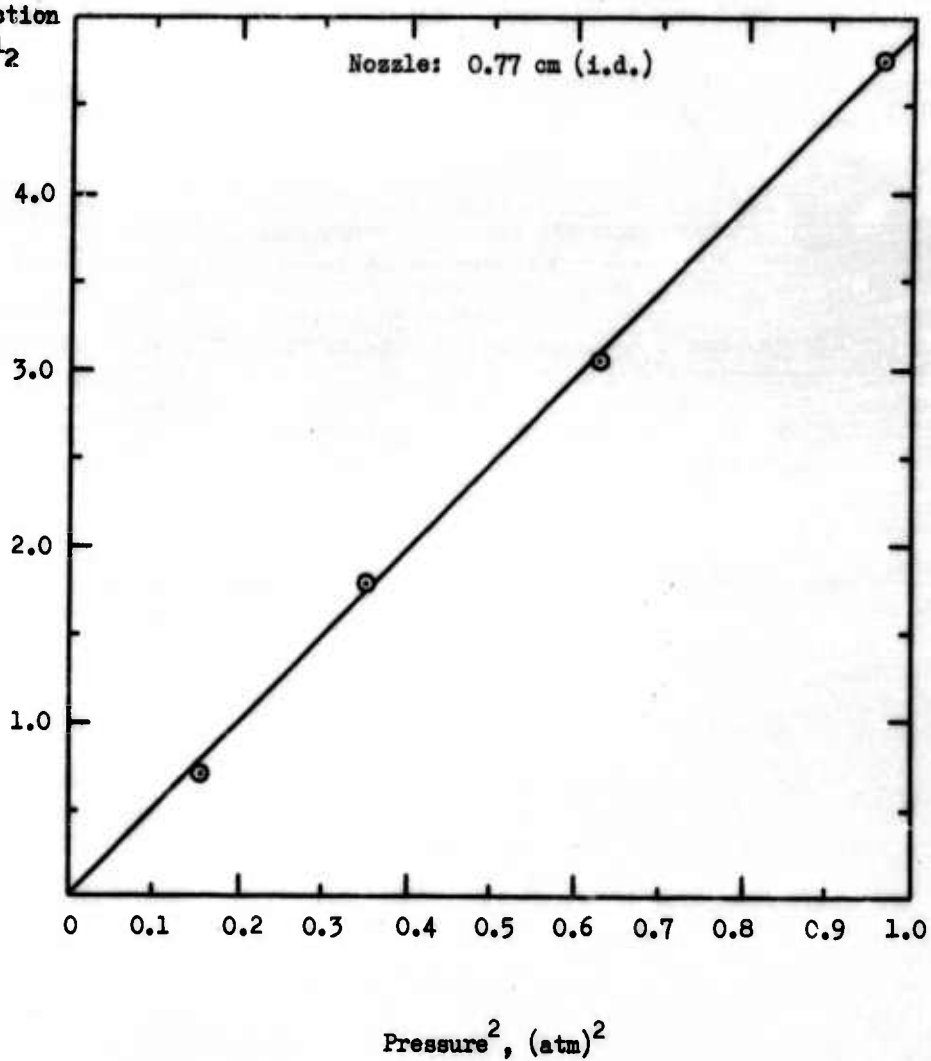


Figure 9

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